Optimising analytical methods for chlorinated paraffins to evaluate their levels in Australia

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Chapter 1

General introduction

Chlorinated paraffins (CPs) is a commonly used term for over 10,000 different polychlorinated *n*-alkanes [1]. CPs are extensively used in numerous applications (e.g. metalworking fluids, plastics, paints and sealants [3]), and produced in large amounts [4]. They have been identified in almost every environmental compartment [5], including remote areas [6]. By comparison, their annual production volume in China alone (ca. 1 million tonnes [7]), is almost equal to that of the cumulative global production volume (ca. 1.3 million tonnes [8]) of a globally banned group of compounds, polychlorinated biphenyls (PCBs), which used to have similar applications (i.e. plastics, paints, sealants [3]). The global annual production must be even higher as information on production volumes is lacking from other suspected large CP producing countries such as Brazil and India.

While they have been identified in many environmental matrices, accurate information on their levels in and potential hazard to the environment, including human, was scarce at the beginning of this PhD study (2014). This was mainly because of the difficulties that arise with the identification and quantification of CPs. CPs are multi-congeneric mixtures, ca. two orders of magnitude more complex than PCBs. Their commercial mixtures might even be more complex because of the presence of other compounds such as iso-paraffins. Just as for PCBs, analytical evidence of the presence of CPs has been available for a number of decades [10], However, in contrast to PCBs, only a limited number of laboratories have the expertise to analyse them accurately. In addition, analysis and quantification are far from standardised and concentrations are often reported as total CPs, or in terms of their groups (i.e. short- (C_{10-13}), medium (C_{14-17}) and long- ($C_{>18}$) chain CPs).

Polychlorinated *n*-alkanes is a more accurate term for CPs, and their current categorisation as groups (i.e. short- (SCCPs), medium- (MCCPs) and long- (LCCPs) chain CPs) is somewhat obsolete, which is elaborated on in Chapter 9. However, as they are currently better known as CPs and their groups, this term is used throughout the thesis.

SCCPs acquired persistent organic pollutant (POP) status by the Stockholm Convention in 2017 [11]. With this POP status, an increasing number of laboratories will need to report comparable and reliable results of SCCPs to authorities. While data are scarce, LCCPs and MCCPs are suspected of resistance to environmental degradation, bioaccumulation and toxic potential [12-15]. Their hazard potential in general remains largely uncertain due to their complexity.

Considering their high production volumes and global distribution, it is essential to accurately quantify their concentrations and assess their potential hazard, especially in regions where their levels are largely unknown. To achieve this, robust analytical capabilities are of critical importance.

1.1 Rationale of the thesis

At the start of this PhD, no peer-reviewed data on CPs in Australia existed and the capability of analysing CPs was lacking, while production of CPs was suspected (i.e. Ixom, Melbourne). The rationale of this thesis was therefore the recognition of the need to advance the capabilities for analysis of CPs in order to allow for the first time a preliminary evaluation of their environmental and human levels in Australia. Based on the rationale for this thesis, there were three aims:

1. Review what is known about the occurrence and properties of these compounds, as well as the challenges and contemporary analytical capabilities.
2. Improve these capabilities by developing and/or adapting two determination methods. Then, evaluating these two techniques, along with the existing techniques, to identify the most suitable one for the purposes of this study.
3. Provide, with the most suitable technique, an initial quantification and evaluation of CP levels in Australia.

1.2 Outline of the thesis

The thesis consists of nine chapters, including this introduction and a concluding chapter. The first three chapters (Chapters 2-4) facilitate the first aim by undertaking critical reviews and four interlaboratory assessments. Chapter 2 critically reviewed what was known about CPs, including their production, environmental levels and fate, while Chapter 3 focused on what the challenges and contemporary capabilities were for analysing CPs before 2015.

Chapter 5 addresses the second aim, in which the performance of two novel and two existing methods for SCCP determination in spiked and naturally contaminated samples was evaluated. In addition, SCCP concentrations in candidate reference materials, thus far unavailable for method validation, were investigated for potential future certification. The newly developed determination method is a comprehensive two-dimensional gas chromatography (GC) method using a micro-electron capture detector (GC×GC-μECD) combined with an optimised quantification method previously applied in another technique (GC coupled to a low-resolution mass spectrometer in electron capture negative ionisation mode, GC-ECNI-LRMS [16, 17]). The other technique is an adaptation of an existing technique, the chlorine-enhanced atmospheric pressure chemical ionisation coupled to a time-of-flight MS (APCI-ToF-HRMS) [18], for the first time combined with the same quantification method mentioned earlier. The two techniques were evaluated along with the most commonly applied technique (GC-ECNI-LRMS) and another technique (carbon skeleton-GC-MS) to identify the most suitable one.

Chapters 6-8 facilitate the third aim. By employing the most suitable method, identified in Chapter 5, these chapters allow a quantification and evaluation of CP levels in a variety of matrices from across Australia with potentially increasing complexity that are available through systematic sampling and archiving programs at Queensland Alliance for Environmental Health Science (QAEHS), Australia. These matrices were sewage sludge from 15 waste water treatment plants (Chapter 6), extracts of passive air samplers deployed for one year at 15 sites covering different land-use (Chapter 7) and stratified pooled serum samples from the Australian Human Biomonitoring Program covering different collection period and age groups (Chapter 8).
Finally, the results are summarised and discussed in Chapter 9, including future perspectives.

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